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ISOLATION AND VALENCY ISOMERIZATION OF CIS-CIS-CIS-1, 3, 5-CYCLONONATRIENE (1, 2)

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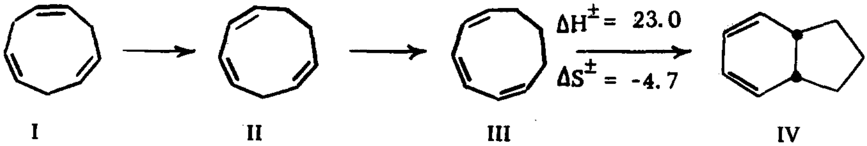
It was reported recently (3) from this Laboratory that cis-cis-cis-1, 4, 7-cyclononatriene I is isomerized by potassium t-butoxide (KOBu) in dimethylsulfoxide (DMSO) to the cis-cis-cis-1, 3, 6-isomer II and then to the bicyclic isomer, (4) cis-bicyclo[4. 3.0]nona-2, 4-diene IV. Although cis-cis-cis-1, 3, 5-cyclononatriene III was not observed, it was suspected to be an intermediate for the formation of IV by valency tautomerism. Since the III → IV valency isomerization is of considerable interest, we sought to detect and actually isolate III. This has proved to be possible, and we have now been able to study directly the III→IV transformation.

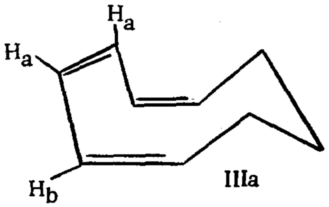


Examination of isomerization solutions of KOBu and 1, 4, 7-triene I in DMSO in an n. m. r. tube at ca. 37.5° reveals the presence of a new olefin formed between the 1, 3, 6-isomer II and bicyclic IV. A typical experiment with 0.85 M KOBu and 0.80 M triene I shows that the concentration of 1, 3, 6-triene II passes through a maximum after ca. 8 minutes, while the concentration of a new species with a sharp vinyl proton signal at τ4.5 reaches a maximum ca. 7 minutes later. In such isomerizations with 1.3 M KOBu at 18°, the triene is predominantly II after 10 minutes and predominantly the new species after 1 hour. Under these conditions further isomerization is relatively slow. By suitable workup of such isomerization mixtures and preparative v. p. c. at 20° the new species can be isolated in a relatively pure state and shown to be cis-cis-cis-1, 3, 5-cyclononatriene III. While the equilibrium proportions of the 1, 4, 7-, 1, 3, 6- and 1, 3, 5-trienes, I, II and III, respectively, have not yet been studied quantitatively, it is clear that the sequence of relative stabilities among the cis-cis-cis-cyclononatrienes is: 1, 3, 5 > 1, 3, 6 > 1, 4, 7.

The new isolated liquid hydrocarbon, n_D^{25} 1.535, with an excellent C, H-analysis for C_9H_{12}, displays an ultraviolet λ_{max} at 296 mμ (ϵ = 4010) in cyclohexane solution (5). In its infrared spectrum in CCl_4 solution the new hydrocarbon displays a band at 1636 cm.$^{-1}$ for the olefinic stretching vibration and a very strong broad band at 669 cm.$^{-1}$ for cis-olefinic C-H out-of-plane deformation, with only very weak absorption in the whole region for trans-olefinic C-H deformation. The n. m. r. spectrum in CCl_4 solution with an external TMS standard shows a multiplet for 6 vinyl protons in the

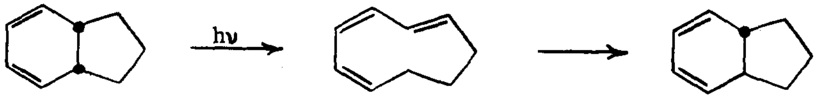
4.2-5.2 τ range, including a relatively sharp singlet at 4.51 τ. A clean multiplet for 4 allylic protons is centered at 7.73 τ and one for 2 methylene protons is centered at 9.00 τ.

The chemistry related to the new hydrocarbon and its spectra are in accord only with the cis-cis-cis-cyclononatriene structure III. Models suggest an extented boat conformation IIIa for this triene and this is borne out by its n.m.r. spectrum. For example, the sharp singlet at 4.51 τ is ascribed to the inner vinyl protons H_a. The H_aH_b torsional angle in conformation IIIa is close to 90° and therefore the coupling between these protons is reduced to a minimum.



IIIa

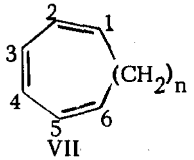
The trans-cis-cis isomer of III, thought to have been obtained by Alder and Dortman (4), has now been isolated by Vogel (8) from photolysis of the bicyclic diene IV. This isomer, namely V, described by Vogel in an adjoining Communication (8), differs from III appropriately in ultraviolet, infrared and n.m.r. spectra.



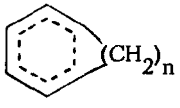
IV V VI

Cis-cis-cis-cyclononatriene III is transformed essentially completely to its valency isomer, cis-bicyclo[4.3.0]nona-2,4-diene IV, in a smooth uncatalyzed thermal reaction. Observation of the pure bicyclic isomer IV, containing less than 0.2% of triene III, for various periods at 100° shows that any equilibrium proportion of III is less than 0.2%. Good first order kinetics were observed for the valency isomerization of III to IV in dilute cyclohexane solution, the reaction being followed by analytical v.p.c. employing an injector temperature of 20° and a column temperature of 5°. Rate constants of $(1.67 \pm 0.05) \times 10^{-4}$ sec.$^{-1}$ at 50.0° and $(7.62 \pm 0.13) \times 10^{-6}$ sec.$^{-1}$ at 25.0° were obtained. These data lead to $\Delta H^{\pm}$ and $\Delta S^{\pm}$ values of 23.0 kcals./mole and -4.7 e.u., respectively. Slightly faster rates with a lower $\Delta H^{\pm}$ are observed by Vogel (8) for the transformation of the isomeric V to the trans-bicyclic VI.

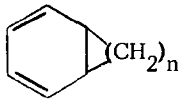
The transformation of III to IV is of interest in the general context of valency tautomerism between a triene VII with six π-electrons and its valency isomer IX with four π- and two σ-electrons by way of a "homobenzene" type (9) transition state VIII. Comparing the III → IV transformation with analogous cases, we see that $\Delta H^{\pm}$ for III → IV is somewhat lower than for the transformations of 1,3,5-cyclooctatriene (9,10) X and cyclooctatetraene (10,11) XII to their bicyclic valency isomers, XI and XIII, respectively. It is also lower than the $\Delta H^{\pm}$ for the conversion of the simplest triene, cis-1,3,5-hexatriene (12) XIV to its valency isomer XV.



VII

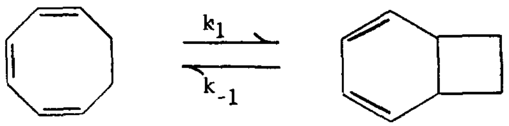


VIII



IX

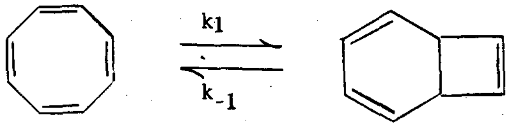
X



XI $\Delta H_{1}^{\pm} = 25.7,\ 26.6;\ \Delta S_{1}^{\pm} = -3,\ -1$

$\Delta H_{-1}^{\pm} = 24.7,\ 25.5;\ \Delta S_{-1}^{\pm} = -2,\ 0$

XII



XIII $\Delta H_{1}^{\pm} = 27.4;\ \Delta S_{1}^{\pm} = -1$

$\Delta H_{-1}^{\pm} = 18.2;\ \Delta S_{-1}^{\pm} = -6$

XIV

XV $\Delta H_{1}^{\pm} = 28.8$

The thermal conversions of cis-cis-cis-III to the cis-bicyclic IV and trans-cis-cis-V to the trans-bicyclic VI are in accord with the stereochemistry visualized by Alder (4). They are also in accord with the stereochemistry of other such transformations in the elegant studies of Vogel (8). This stereochemistry has been explained by Hoffmann (13) with the rationale that C_1- C_6 bond formation involves initially p-lobes of the same sign on C_1 and C_6 in the highest occupied molecular orbital in the ground state of the triene π-electron system. The photochemical conversion of the cis-bicyclo[4.2.0]nonadiene IV to trans-V observed by Vogel (8) is in line with other indications (8, 14-16) that the preferred stereochemistry of the photolytic interconversion of triene and its diene valency isomer tends to be the reverse of that which obtains in the thermal reaction. This is accounted for with Hoffmann's molecular orbital rationale (13) matching up p-lobes of the same sign on C_1 and C_6 in the highest occupied molecular orbital in the triene excited state (17).

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(1) Research was supported in part by a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgement is hereby made to the donors of this fund.

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(3) J. W. H. Watthey and S. Winstein, J. Am. Chem. Soc. 85, 3715 (1963).

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(13) R. Hoffmann, Eighth Annual Organic Chemistry Conference, U. S. Army Natick Laboratories, Natick, Mass., October 13-14, 1964.

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(17) See ref. 14 for the similar suggestion by Oosterhoff that the stereochemistry may depend on the symmetry characteristics of the highest occupied π-orbital of the triene system.